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Effect of SO_2 and NO_2 on corrosion and solid formation in dense phase CO_2 pipelines

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Abstract

CO_2 has been transported and used for EOR (Enhanced Oil Recovery) for more than 30 years with a good track record. Based on the good experiences it seems to be generally accepted that corrosion will be insignificant in CO_2 transport pipelines as long as the water content is well below the water solubility. The solubility in pure CO_2 at 100 bar is about 1900-3200 ppmv in the temperature range 4-25 °C. There is no consensus on what the actual target concentration for the maximum water content should be in the CO_2 to be transported, but it is often referred to 500 ppmv in the CCS (Carbon Capture and Storage) literature. The question is whether this apparently safe water level also applies when glycols, amines and flue gas contaminants like SO_x, NO_x and O_2 are present in moderate amounts. These impurities dissolve readily in water and induce an aqueous phase at a much lower water concentration than the solubility limits reported for pure CO_2 and CO_2 contaminated with hydrocarbons. When SO_2, water and O_2 are present sulphurous and/or sulphuric acid (H_2SO_3 and H_2SO_4) might form. The minimum water concentration required for acid formation is not known, but the presence of $FeSO_3$ and/or $FeSO_4$ seen on steel surfaces exposed in dense phase CO_2 at low water content (less than 500 ppmv) shows that corrosion takes place when 100-344 ppmv SO_2 is present. The corrosion rate was further increased when NO_2 was added to the system. Rotating autoclave experiments run with steel exposed to 100 bar CO_2, 488 and 1220 ppmv water and 96-478 ppmv NO_2 resulted in weight loss corrosion rates of 0.05-1.6 mm/year.Typically less than 5% of the added impurities were apparently consumed by corrosion in the NO_x and SO_x experiments before the corrosion rate slowed down. The difference in the impurity concentration at start up and when the experiment was terminated was much larger than the consumption estimated from corrosion. The impurities became apparently “non-active” during the exposure and it can be questioned if the measured corrosion rates in the present experiments and in other reported lab experiments reflect the worst case conditions in the pipeline. The experimental observations so far support the need for a dynamic test system with replenishment of impurities and instant (continuous) analyses of the dissolved impurity concentrations. Such dynamic tests are required in order to define acceptable CO_2 specifications with confidence.

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Keywords: Carbon steel; corrosion;dense phase CO_2; impurities; H_2O;NO_2; H_2S; O_2

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1. Introduction

Following the "Blue Map Scenario" [1] for the abatement of climate change, about 10 Gtons/year (10^{12} kg/year) of CO_2 need to be safely transported and stored underground in 2050. This requires the construction of about 3000 twelve-inch (or 1000 twenty-inch) pipelines assuming a flow velocity of 1.5 m/s. The only cost effective material that can be used for such an extensive network is carbon steel.

There are currently no recognized specifications for the CO_2 quality required for pipeline transport, and it is possible that when specifications eventually are established, the required CO_2 quality may vary depending on the end target (EOR, storage in aquifers or other storage) and legislation differences. The main technical constraint will be the maximum allowable impurity content in CO_2 to be injected or the impurities that can be allowed from a corrosion and safety point of view (rupture) during pipeline or ship transport.

A number of tentative CO_2 specifications have been suggested [2,3,4,5]. The two most referred to are the DYNAMIS specification shown in Table 1 and the specifications for dried CO_2 issued by the Intergovernmental Panel on Climate Change-IPCC (Table 2).

Table 1. DYNAMIS CO_2 quality recommendation [2]

Component	Concentration	Limitation
H_2O	500 ppmv	Technical
H_2S	200 ppmv	Health & safety
CO	2000 ppmv	Health & safety
O_2	Aquifer < 4 vol%, EOR 100 – 1000 ppmv	Technical
CH_4	Aquifer < 4 vol%, EOR < 2 vol%	
N_2, Ar, H_2	< 4 vol % (all non-condensable gases)	
SO_x	100 ppmv	Health & safety
NO_x	100 ppmv	Health & safety
CO_2	>95.5 vol %	

Table 2. Concentrations of impurities in dried CO_2 suggesed by IPCC [3]

	SO_2 ppmv	NOx ppmv	H_2S ppmv	CO ppmv	N_2 /Ar/O_2 ppmv
COAL FIRED PLANTS					
Post- combustion capture	<100	<100	0	0	100
Pre-combustion capture	0	0	100-6000	300-4000	300-6000
Oxy-fuel	5 000	100	0	0	37 000
GAS FIRED PLANTS					
Post-combustion capture	<100	<100	0	0	100
Pre-combustion capture	0	0	<100	400	13000
Oxy-fuel	<100	<100	0	0	41000

A large variation is seen in these specifications and it is reasonable as the impurities in the CCS (Carbon Capture and Storage) stream will depend on the fuel type, the energy conversion process (post-combustion, pre-combustion or oxyfuel) and the capture process. In addition, with new capturing technologies, new compounds (impurities) can be formed and higher concentration of impurities can follow the CO_2 phase with unknown effect on corrosion. When pipeline design philosophy for CO_2 transportation is discussed it is commonly accepted that the CO_2 should be sufficiently dry to prevent

drop-out of a separate aqueous phase in any part of the pipeline, as free water can give both corrosion and hydrate formation. There is however no consensus on what the actual target for the maximum water concentration should be. It has been argued that full dehydration down to 50 ppmv should be applied. This limit has been specified for the first CO_2 pipelines in the USA [6] and for the Snøhvit [8] pipeline in Norway. Other specifications are less conservative as suggested in the DYNAMIS project (500 ppmv) and for the Kinder Morgan pipeline [4] (650 ppmv). All the suggested values are well below the water solubility for pure dense phase CO_2 given in Figure 1.

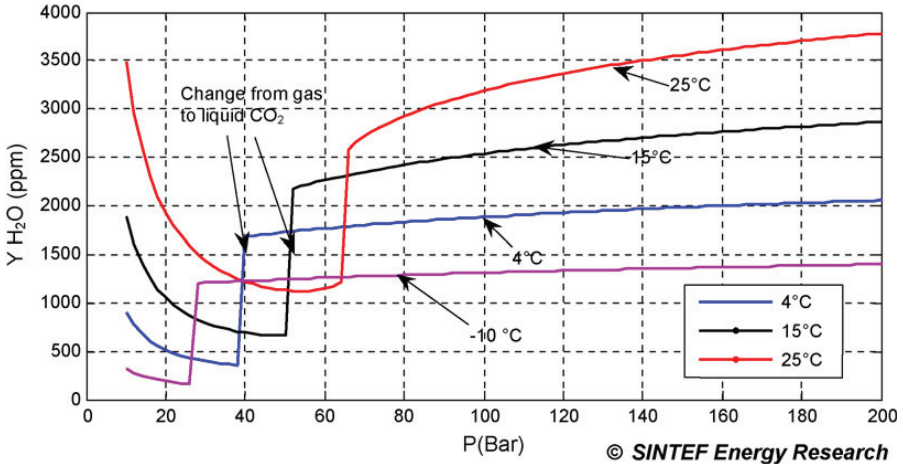

Figure 1. Water solubility in pure CO_2 [2]

The motivation for the present work was the expectation that water can precipitate at much lower water content when impurities like amine, glycol, SO_x and NO_x are present. These impurities will dissolve readily in water and give an aqueous phase at a much lower water concentration than the solubility limits reported for pure water and CO_2. No water solubility data for these systems have been found in the literature and corrosion experiments were therefore run with SO_2 and NO_2 to check the validity of the 500 ppm water limit suggested in for instance the DYNAMIS recommendation. The experiments were run at 100 bar and 25 °C, condition giving a water solubility of about 3200 ppmv in the pure water-CO_2 system (see Figure 1).

Most of the data and the text in the present paper have also been presented recently at the EUROCORR 2012 conference [7].

2. Experimental

There are no recognized standards for corrosion testing in dense phase CO_2 with impurities. The data published in the literature are based on autoclave experiments performed under stagnant conditions or with rotating cages [8]. The main experimental challenge is impurity control. The volume of the corrosive phases that might form in a system with a few hundred ppmv of impurities is very small. The volume fraction is $< 10^{-4}$ (< one droplet per litre) and key issues are the consumption of the impurities during the exposure and to which degree the corrosive phase actually reaches the exposed steel specimens in the autoclave experiments, particularly in stagnant experiments.

Figure 2. Left: Slim autoclaves rotated in a thermal cabinet. Right: Carbon steel specimens (OD 10 mm, length 10mm) mounted in a 8-10 cm long sliding specimen rack

IFE uses an experimental set up for dense phase CO_2 testing where slim (ID 20-30 mm) autoclaves are rotated on a shaft inside a temperature controlled chamber (see Figure 2). The temperature can be varied from 0-50 °C. The rotating device can accommodate 5 long (2 m) and 4 short (0.6 m) autoclaves. The test specimens are mounted on small cylindrical racks that slide from one end to the other when the autoclave rotates. This gives good mixing and disturbed flow around the test specimen. The rack weight determines the maximum flow velocity. The autoclaves can be rotated continuously at various speeds or in steps according to a programmed sequence. The rotation speed was 3 revolutions per minute in the present experiments, corresponding to an average flow velocity of 0.2 m/s and a peak flow velocity around 1 m/s.

The benefit and shortcomings of the rotating autoclave approach compared to fixed autoclaves and closed loops are:

Benefits: Easy and cheap to operate, simple geometry. Several autoclaves can be run in parallel. Most important; few dead ends where impurities forming a minute separate water rich phase can be trapped.

Shortcomings: The flow velocity and the flow direction are alternating. Renewal and control of test liquid is difficult during the exposure, but low corroding surface area to liquid volume will reduce the need for adjustment of the liquid composition.

The corrosion rate was determined from weight loss. The accuracy of the weighing is about 0.1 mg and this corresponds to a corrosion rate of 0.002 mm/y in a 1 week exposure. An error (inaccuracy) is also introduced when the corrosion film is stripped as a tiny amount of steel is removed. This gives a practical detection limit of 0.01 and 0.005 mm/y respectively for exposures shorter and longer than 1 week.

The cylindrical steel specimens (10 mm long, OD 10 mm) were machined from ferritic-pearlitic X65 pipeline steel with the composition shown in Table 3.

A known amount of impurities were added to the autoclaves at start up and the reported concentrations are the nominal concentrations at start up. The consumption rate and the changes in the concentration of impurities due to other reactions were not measured during the experiments.

Table 3. Element analysis (wt-%) of the exposed steel specimens

Steel	C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
API 5L X65	0.08	0.25	1.54	0.001	0.019	0.04	0.05	0.095	0.01	0.02	0.038	0.001	0.043

3. Results and discussion

Test conditions and results are summarized in Table 4. Four groups of experiments were run, all at 100 bar and 25 °C:

Experiment W1 and W2: No impurity apart from water
Experiment SW1, SW2 and SW3: SO_2 and water
Experiment NW1, NW2, NW3 and NW4: NO_2 and water
NSW1: NO_2, SO_2 and water

The water concentration at start-up was either 488 ppmv which is slightly below the maximum water concentration given in the DYNAMIS table (Table 1) or 1220 ppmv.

Table 4. Test conditions and results for all corrosion tests run in rotating autoclaves

Exp. No:	Temp °C	Pressure bar	H_2O ppmv	SO_2 ppmv	NO_2 ppmv	Exposure days	Rotation r/min	Type of attack	Corr.rate mm/y
W1	25	~100	488			14	3	-	No
W2	25	~100	1222			14	3	-	No
SW1	25	~100	488	100		14	3	Spots	<0.005
SW2	25	~100	488	344		14	3	Spots	<0.005
SW3	25	~100	1220	344		14	3	Spots	0.02
NW1	25	~100	1220		478	10	3	Uniform	1.6
NW2	25	~100	1220		191	10	3	Uniform	0.67
NW3	25	~100	488		191	20	3	Uniform	0.06
NW4	25	~100	488		96	3	3	Uniform	0.17
NSW 1	25	~100	488	138	191	7	3	Uniform	0.017

3.1. Water only experiments (W1 and W2)

No attack was observed at either 488 or 1220 ppm water. This is in accordance with previously published lab experiments run under stagnant conditions and field experiences [8].

3.2. SO_2 experiments (SW1, SW2 and SW3)

The exposed steel specimens were slightly stained all over and spots with deeper attacks were randomly distributed as shown in Figure 3 and Figure 4. The average corrosion rate was low, <0.005, <0.005 and 0.02 mm/y respectively. Since the attacks were localised covering less than 10% of the surface, it is reasonable to assume that the local corrosion can be at least 5-10 times higher than the average rate. The depth of the spot wise attack was less than 3 µm and difficult to measure accurately. 3 µm correspond to a corrosion rate of about 0.08 mm/y.

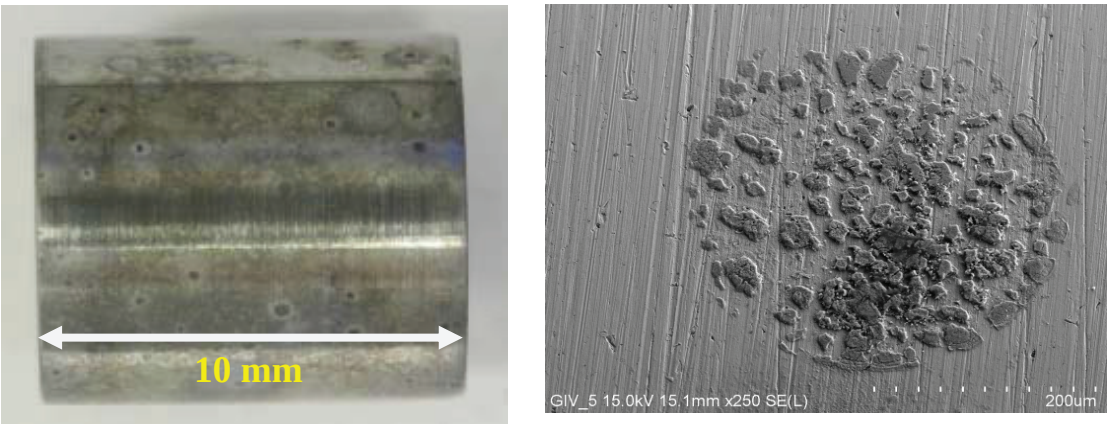

Figure 3. Specimen exposed in experiment SW 2

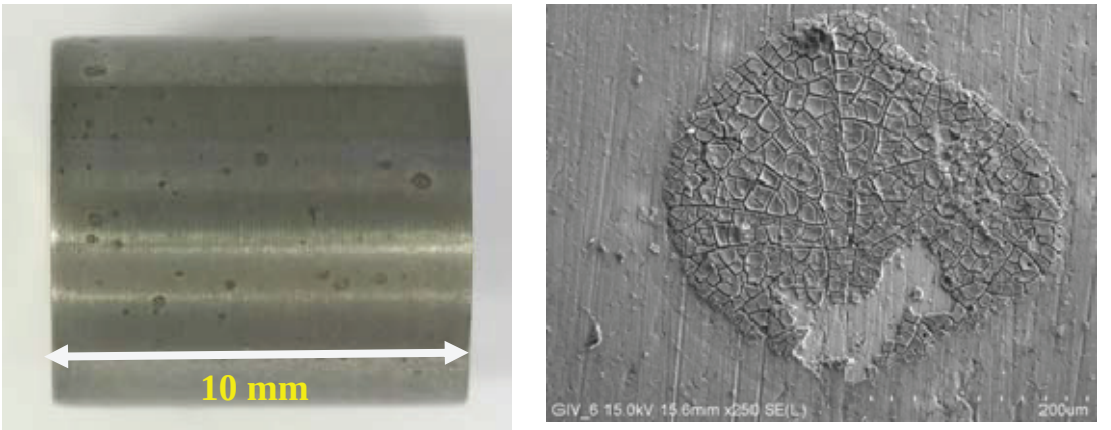

Figure 4. Specimen exposed in experiment SW 3

The attacked area was covered with blackish corrosion products. The composition of the corrosion film was analysed with EDS (Energy-dispersive X-ray spectroscopy). The O_2 concentration was more than 4 times higher than the sulphur concentration. Indicating that that $FeSO_4(xH_2O)$ or $FeSO_3(xH_2O)$ forms on the surface.

The corrosion mechanisms have not been studied in any detail. The sulphur chemistry and the effect of sulphur containing components on the corrosion mechanism are considered to be very complex. SO_2 and water are assumed to form sulphurous acid (H_2SO_3) that can be oxidised and form H2SO4, particularly when O2 is present. The possible presence of FeSO4 in both previous reported [10],[11] experiments run with SO_2 and O_2 and in the present experiments run with SO_2 only indicates that oxidation happened.

The minimum water concentration required for H_2SO_3 and H_2SO_4 formation is not known, but the presence of $FeSO_4/FeSO_3$ on the corroded surface shows that a corrosive phase forms at water concentrations far below the water solubility reported for the pure water-CO_2 system. The lowest water concentration tested was 488 ppmv and the corrosion product film morphology both at this concentration and higher concentrations indicates that small droplets attached to the surface and gave localised attack.

3.3. NO_2 experiments (NW1, NW2, NW3, NW4)

Four experiments were run with various water and NO_2 contents. The weight loss corrosion rates were much higher (0.06-1.6 mm/year) than in the SO_2 experiments run at similar impurity concentrations. The specimens were evenly corroded and got a blackish/orange coloured dusty film on the surface (Figure 5). The dust was mobilised and spread around in the autoclave. EDS analyses of the dusty product indicated Fe and O only, no N containing compounds were found. XRD (X-ray Diffraction) analyses gave poor signals and no positive identification of crystalline products.

The corrosion rate decreased with decreasing water and NO_2 content as indicated in Figure 6. The higher measured corrosion rate in the experiment (NW4) with 96 ppmv NO_2 and 488 ppmv water compared to the experiment (NW3) with 191 ppmv is attributed to the much lower duration that gives less consumption of reactants. The experiments were run 3-20 days and the consumption of water and NO_2 might have been significant. It is likely that the reported corrosion rates would have been much higher if water and NO_2 were replenished at the same rate as they were consumed.

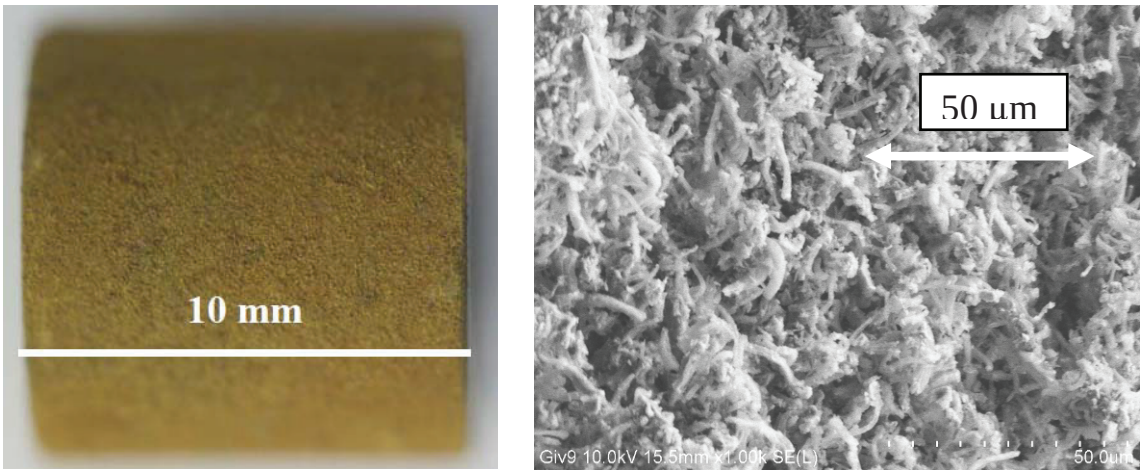

Figure 5. Specimen exposed in experiment NW1

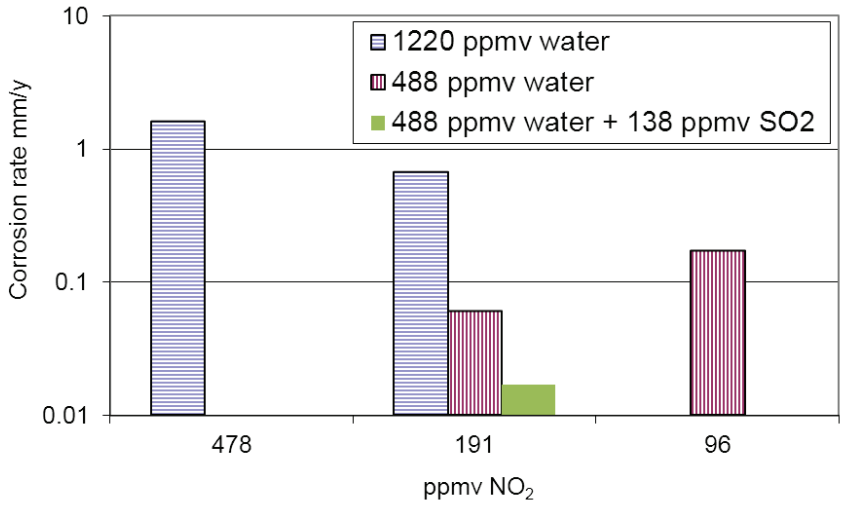

Figure 6. Corrosion rates measured in experiments with NO_2

The corrosion mechanism has not been studied in any detail. It should be noted that NO_2 is highly soluble in water and reacts with water to produce nitric acid and NO under atmospheric conditions:

$$3\ NO_2(g) + H_2O(l) \text{ ---> } 2\ HNO_3(aq) + NO(g) \quad (1)$$

It is likely that the same type of reaction occurs in the dense phase CO_2 system. The experimental results indicate that the nitric acid oxidises Fe^{2+} and give the rust-like dusty product observed in the experiment. The corrosion product film which is apparently very fluffy does not offer much protection and that can explain the much higher corrosion rate in the NO_2 experiments compared to that seen in SO_2.

3.4. SO_2 and NO_2 experiment

Experiment NSW1 was run with a combination of SO_2, NO_2 and water and in a shorter autoclave (about 60 cm) than the autoclaves (about 2 m) used for the other experiments. The weight loss corrosion rate was 0.017 mm/year, significantly less than in the other experiments run with the same NO_2 concentration. Whether the lower corrosion rate is attributed to less available impurities in the short autoclave, protective corrosion product film formed on the steel surface or consumption of impurities due to impurity reactions in the bulk phase can be questioned. More experiments are needed to sort out the mechanism and possibility that the corrosion rate is lower for certain combination of impurities than for the single components.

3.5. Worst case corrosion rate

The consumption rate of impurities due to corrosion depends on the corrosion rate, the steel surface to dense phase CO_2 volume ratio and the corrosion mechanism. The H_2O, SO_2, NO_2 consumption will in most cases be 1 mol per 1 mol corroded iron and the expected consumption rate in a closed system is

shown in Figure 7. If the corrosion rate is high (> 0.1 mm/year) the consumption might be so fast that it will either be necessary to add controlled amounts of water/SO_2/NO_2 during exposures lasting more than one day or use a very small steel surface to liquid volume ratio.

The actual consumption rate of impurities has been studied in autoclave experiments at IFE. Typically less than 5% of the added impurities are apparently consumed by corrosion in NO_x and SO_x experiments before the corrosion rate slows down. The difference in the impurity concentration at start up and when the experiment is terminated is much larger than the consumption estimated from corrosion. The observation that a large part of the impurities become "non-active" during the exposure can have several reasons:

Immobilization: The corrosive phase can be trapped in dead legs or wet the autoclave walls preferentially.

Some of the impurities will react with other impurities and thus slowly change to other products that are less corrosive or more easily immobilised; e.g. formation of elemental sulphur from H_2S ($H_2S + O_2 = S + H_2O$), oxidation of H_2SO_3 to H_2SO_4, formation of NO_2 from NO and O_2.

The corrosion rate slows down with time due to the formation of protective corrosion product layers on the surface. This might to a certain degree explain reduced corrosion with time, but not the reduced concentration of impurities measured when experiments are finished.

Based on the results it can be questioned if the measured corrosion rates in the present experiments and in other reported lab experiments reflect the worst case conditions in the pipeline. The experimental observation so far supports the need for a dynamic test system with replenishment of impurities and instant (continuous) analyses of the dissolved impurity concentrations. Such dynamic tests are required in order to define acceptable CO_2 specifications with confidence.

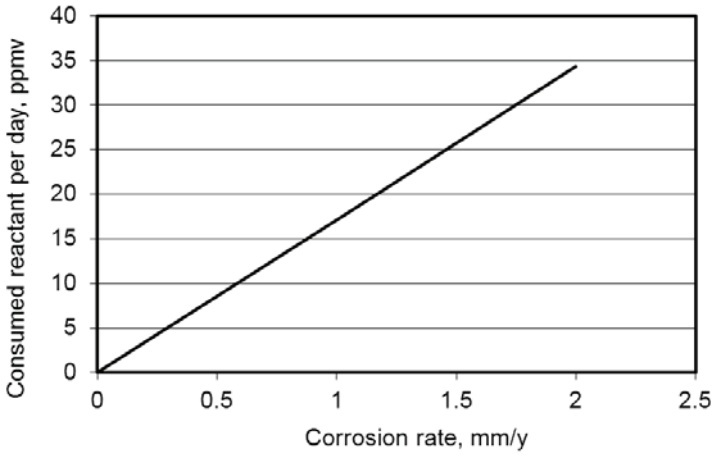

Figure 7. Consumption rate per day of water, SO_2, and NO_2 when 10 cm^2 steel is exposed in 1 kg dense phase CO_2. It is assumed that 1 mol Fe consumes 1 mol impurity

3.6. Solid formation

Formation of solid particles due to corrosion or redox reactions in the bulk phase (e.g. sulphur from H_2S and O_2) may have severe consequences for the pipeline, but perhaps even more so at the interface

between the transport and the storage system. These processes may cause reservoir clogging and reduce the injectivity.

The amount of solids that forms when e.g., 1 ppmv H_2O reacts with the pipe wall and form $FeCO_3$ amounts to 25 t/year and a 0.1 mm corrosion product thick layer on the pipe wall corresponds to about 50 tons solids in a 100 km long 20" pipeline transporting dense phase CO_2 at 1.5 m/s. A key question will be to which degree the corrosion products stick to the wall or become mobilised. Some products might grow on the wall for a long time and eventually spall off. Such products might form larger flakes (mm scale) while other products are more dust-like and detach easily. Dust-like products have been observed particularly in experiments with NO_2 (see Figure 5) where the dust came out of the autoclave when the system was vented.

4. Conclusion

Field experience and most lab experiments show that dry pure CO_2 and pure CO_2 that contains dissolved water well below the saturation limit in the pure CO_2-H_2O system is non-corrosive to carbon steel under transportation pipeline operation conditions.

There is very little published data on the effect of impurities like SOx, and NOx. Experiments have shown that corrosion takes place at a water concentration far below the water solubility in the pure water-CO_2 system. Particularly large effect and high corrosion rates (> 1 mm/y) were seen in the presence of NO_2.

There is a strong need to better understand the relation between the water content and the concentration of the impurities. At present, there is a lack of data and therefore it is not possible to define the limits for the various impurities when they are mixed.

Corrosion products and other solid reaction products mobilized in the dense phase CO_2 stream can affect the injectivity in the reservoir. Therefore it might be necessary to quantify the amount of corrosion products that will remain on the steel wall and identify the type and amount of solids that will be mobilized and follow the CO_2 stream.

A few % only of the added impurities were used for corrosion in the present experiments. The impurities became apparently "non-active" during the exposure and it can be questioned if the measured corrosion rates in the present experiments and in other reported lab experiments reflect the worst case conditions in the pipeline. The experimental observations so far support the need for a dynamic test system with replenishment of impurities and instant (continuous) analyses of the dissolved impurity concentrations. Such dynamic tests are required in order to define acceptable CO_2 specifications with confidence

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